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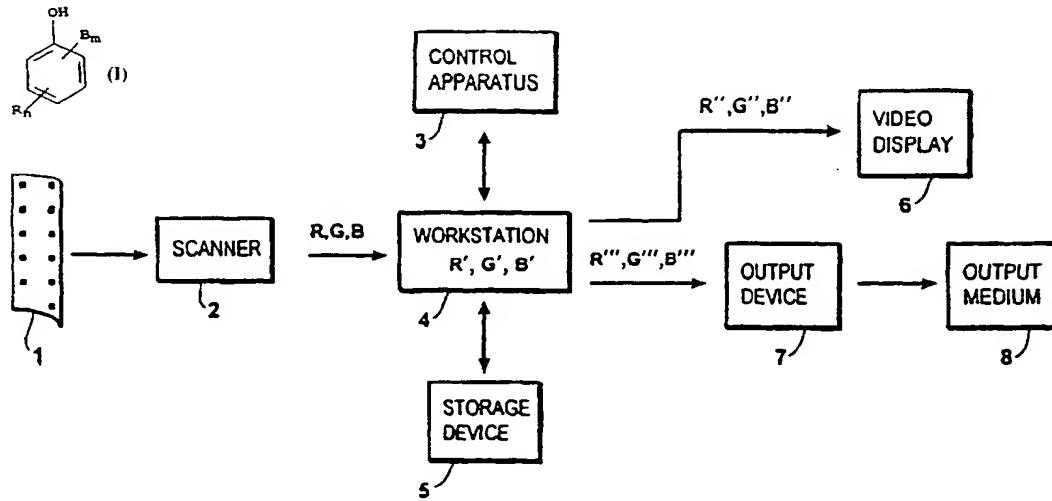
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(54) Title: COLOR PHOTOTHERMOGRAPHIC ELEMENTS COMPRISING PHENOLIC THERMAL SOLVENTS



(57) Abstract: A color photothermographic element comprising at least three light-sensitive units which have their individual sensitivities in different wavelength regions, each of the units comprising at least one light-sensitive silver-halide emulsion, binder, and dye-providing coupler, and a blocked developer in the presence of a thermal solvent represented by the structure (I), wherein the groups are as defined in the specification to promote the thermal development of the photothermographic element.

## INTERNATIONAL SEARCH REPORT

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PCT/US 01/16890

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03C1/498 G03C1/42 G03C7/28 G03C8/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 1 113 324 A (EASTMAN KODAK CO) 4 July 2001 (2001-07-04) paragraph '0170!; example 7 ---	1-44
E	EP 1 113 316 A (EASTMAN KODAK CO) 4 July 2001 (2001-07-04) abstract; example 6 paragraph '0179!; example 7 ---	1-44
X	US 5 436 109 A (BAILEY DAVID S ET AL) 25 July 1995 (1995-07-25) column 9, line 60 -column 10, line 19 column 13, line 40 - line 53 claim 1 ---	1-44 -/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 468 587 A (BAILEY DAVID S ET AL) 21 November 1995 (1995-11-21) column 16, line 68 -column 17, line 50; claims 26,31,36 column 18, line 59 - line 68 column 23, line 17 -column 24, line 10 ---	1-44
X	DATABASE WPI Section Ch, Week 198730 Derwent Publications Ltd., London, GB; Class E19, AN 1987-209836 XPO02186383 & JP 62 136645 A (KONISHIROKU PHOTO IND CO LTD), 19 June 1987 (1987-06-19) abstract * compounds 5,8,9,22,23 * ---	1-44
A	EP 0 573 048 A (KONISHIROKU PHOTO IND) 8 December 1993 (1993-12-08) page 36, line 49 - line 55 page 37, line 35 - line 42 page 37, line 56 -page 38, line 14 * page 33, compound TS-3 * -----	1

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 01/16890

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Silver (from silver salt SS-2)	0.32 g/m <sup>2</sup>
Coupler M-1 (from coupler dispersion Disp-1)	0.54 g/m <sup>2</sup>
Developer Dev-1	0.86 g/m <sup>2</sup>
Melt Former	Equimolar to salicylanilide at 0.86 g/m <sup>2</sup>
Lime-processed gelatin	4.3 g/m <sup>2</sup>

*Common Components*

*Silver salt dispersion SS-1:*

A stirred reaction vessel was charged with 431 g of lime-processed gelatin and 6569 g of distilled water. A solution containing 214 g of benzotriazole, 2150 g of distilled water, and 790 g of 2.5 molar sodium hydroxide was prepared (Solution B). The mixture in the reaction vessel was adjusted to a pAg of 7.25 and a pH of 8.00 by additions of Solution B, nitric acid, and sodium hydroxide as needed.

A 4 L solution of 0.54 molar silver nitrate was added to the kettle at 250 cc/minute, and the pAg was maintained at 7.25 by a simultaneous addition of solution B. This process was continued until the silver nitrate solution was exhausted, at which point the mixture was concentrated by ultrafiltration. The resulting silver salt dispersion contained fine particles of silver benzotriazole.

*Silver salt dispersion SS-2:*

A stirred reaction vessel was charged with 431 g of lime-processed gelatin and 6569 g of distilled water. A solution containing 320 g of 1-phenyl-5-mercaptotetrazole, 2044 g of distilled water, and 790 g of 2.5 molar sodium hydroxide was prepared (Solution B). The mixture in the reaction vessel was adjusted to a pAg of 7.25 and a pH of 8.00 by additions of Solution B, nitric acid, and sodium hydroxide as needed.

A 4 l solution of 0.54 molar silver nitrate was added to the kettle at 250 cc/minute, and the pAg was maintained at 7.25 by a simultaneous addition of

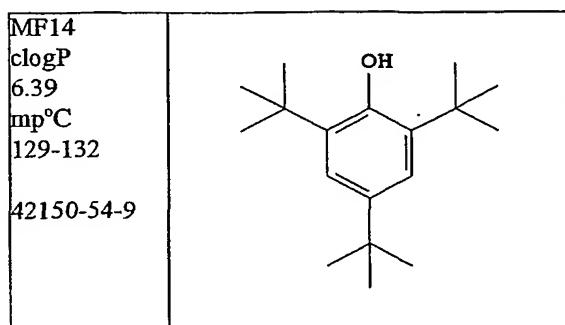
solution B. This process was continued until the silver nitrate solution was exhausted, at which point the mixture was concentrated by ultrafiltration. The resulting silver salt dispersion contained fine particles of the silver salt of 1-phenyl-5-mercaptotetrazole.

5 *Emulsions:* The silver halide emulsion was prepared by conventional means to have the following morphology and composition. The emulsion was spectrally sensitized to green light by addition of sensitizing dyes and then chemically sensitized for optimum performance.

10 E-1: a tabular emulsion with composition of 96% silver bromide and 4% silver iodide and an equivalent circular diameter of 1.2 microns and a thickness of 0.12 microns.

*Melt Former Dispersion:*

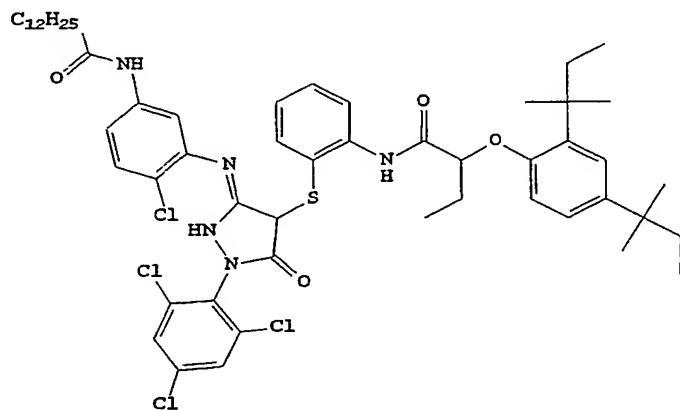
15 A dispersion of salicylanilide was prepared by the method of ball milling. To a total 20 g sample was added 3.0 g salicylanilide solid, 0.20 g poly(vinyl pyrrolidone), 0.20 g TRITON X-200 surfactant, 1.0 g gelatin, 15.6 g distilled water, and 20 ml of zirconia beads. The slurry was ball milled for 48 hours. Following milling, the zirconia beads were removed by filtration. The slurry was refrigerated prior to use. For preparations on a larger scale, the salicylanilide was media-milled to give a final dispersion containing 30%  
20 Salicylanilide, with 4% TRITON X-200 surfactant and 4% poly(vinyl pyrrolidone) added relative to the weight of salicylanilide. In some cases the dispersion was diluted with water to 25% salicylanilide or gelatin (5% of total) was added and the concentration of Salicylanilide adjusted to 25%. If gelatin is added, biocide (KATHON) is also added. Melt dispersions of the melt formers  
25 (thermal solvents) having the specified structures MF1 to MF22 were prepared, including the following comparatively ineffective melt former MF-14:



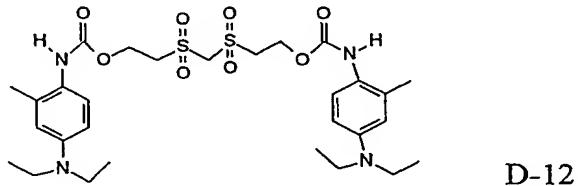
*Coupler Dispersion Disp-1:*

An oil based coupler dispersion was prepared containing coupler M-1, tri-cresyl phosphate and 2-butoxy-N, N-dibutyl-5-(1,1,3,3-tetramethylbutyl)-benzenamine, at a weight ratio of 1:0.8:0.2.

**Coupler M-1**



**10 Incorporated Developer (Dev-1):**



*Developer Dispersion DD-1:*

This material was ball-milled in an aqueous mixture, for 4 days using Zirconia beads in the following formula. For 1g of incorporated developer, sodium tri-isopropylnaphthalene sulfonate (0.1 g), water (to 10 g), and beads (25 ml), were used. In some cases, after milling, the slurry was diluted with warmed 5 (40°C) gelatin solution (12.5%, 10 g) before the beads were removed by filtration. The filtrate (with or without gelatin addition) was stored in a refrigerator prior to use.

*Coating Evaluation:*

The resulting coatings were exposed through a step wedge to a 10 3.04 log lux light source at 3000K filtered by Daylight 5A, 0.6 Inconel and Wratten 9 filters. The exposure time was 0.1 seconds. After exposure, the coating was thermally processed by contact with a heated platen for 20 seconds. A number of strips were processed at a variety of platen temperatures in order to 15 check the generality of the effects that were seen. From the density readings at each step, two parameters were obtained:

- A. Onset Temperature,  $T_o$ : Corresponds the temperature required to produce a maximum density ( $D_{max}$ ) of 0.5. Lower temperatures indicate more active developers which are desirable.
- B. Peak Discrimination,  $D_p$ : For the optimum platen temperature, the peak 20 discrimination corresponds to the value:

$$D_p = \frac{D_{max} - D_{min}}{D_{min}}$$

Higher values of  $D_p$  indicate melt formers producing enhanced signal to noise, which is desirable.

25 The coatings listed above performed as shown in the Table 2 below.

TABLE 2

Coating	Melt Former	Laydown	T <sub>o</sub> (°C)	D <sub>P</sub>
I-1	MF-1	0.86 g/m <sup>2</sup>	136	14.7
I-2	MF-2	0.90 g/m <sup>2</sup>	139	15.1
I-3	MF-3	0.86 g/m <sup>2</sup>	143	22.4
I-5	MF-4	0.86 g/m <sup>2</sup>	143	6.3
I-6	MF-5	0.86 g/m <sup>2</sup>	141	15.0

The data show consistently good onset temperatures and discriminations which are characteristics of effective melt formers.

Samples of unexposed coatings I-1 to I-6 were conditioned to 50% relative humidity and then incubated for 4 weeks at 38°C in sealed envelopes. The density formation after exposure and processing was compared to samples conditioned to 50% relative humidity and kept in a freezer. The difference in Dmin values (test-freezer check) are tabulated below in Table 3. They show consistently small changes in Dmin.

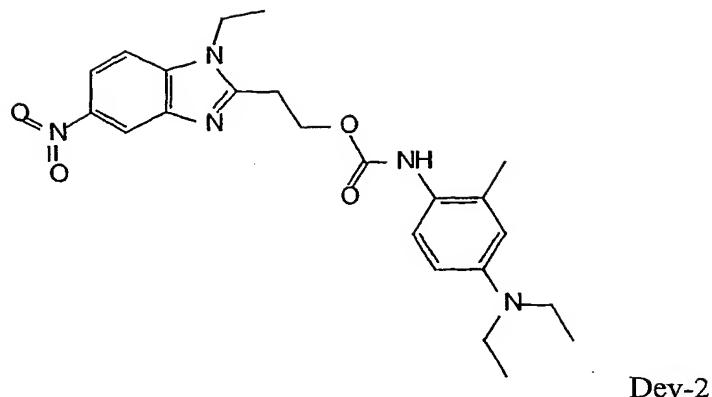
10

TABLE 3

Coating	Melt Former	Laydown	Δ Dmin
I-1	MF-1	0.86 g/m <sup>2</sup>	0.13
I-2	MF-2	0.90 g/m <sup>2</sup>	0.09
I-3	MF-3	0.86 g/m <sup>2</sup>	0.03
I-5	MF-4	0.86 g/m <sup>2</sup>	0.03
I-6	MF-5	0.86 g/m <sup>2</sup>	0.09

## EXAMPLE 2

Coatings were made using the same format as for Example 1 except the developer used was Dev-2 (D-3), coated at 1.18 g/m<sup>2</sup>



Data from these coatings is shown in the following Table 4.

TABLE 4

Coating	Melt Former	Laydown	T <sub>g</sub> (°C)	D <sub>P</sub>
I-7	MF-1	0.65 g/m <sup>2</sup>	134	8.1
I-8	MF-2	0.69 g/m <sup>2</sup>	137	10.1
I-9	MF-3	0.65 g/m <sup>2</sup>	148	9.7
I-10	MF-4	0.80 g/m <sup>2</sup>	144	3.4
I-11	MF-5	0.65 g/m <sup>2</sup>	140	7.3

5

Samples of unexposed coatings I-1 to I-6 were conditioned to 50% relative humidity and then incubated for 4 weeks at 38°C in sealed envelopes. The density formation after exposure and processing was compared to samples conditioned to 50% relative humidity and kept in a freezer. The differences in 10 Dmin values are tabulated in TABLE 5 below.

TABLE 5

Coating	Melt Former	Laydown	Δ Dmin
I-7	MF-1	0.65 g/m <sup>2</sup>	0.17
I-8	MF-2	0.69 g/m <sup>2</sup>	0.23

I-9	MF-3	0.65 g/m <sup>2</sup>	0.09
I-10	MF-4	0.80 g/m <sup>2</sup>	0.08
I-11	MF-5	0.65 g/m <sup>2</sup>	0.20

### EXAMPLE 3

This example illustrates the use of various thermal solvents according to the present invention. Coatings were made using the same format as 5 for Example 1 except the laydowns of all components, emulsion and dispersions used in all layers, were increased by 30% as indicated in Table 6 below.

TABLE 6

Coating	Melt Former	Laydown	T <sub>o</sub> (°C)	D <sub>P</sub>
I-12	MF-1	1.12 g/m <sup>2</sup>	134	13.3
I-13	MF-2	1.19 g/m <sup>2</sup>	135	8.4
I-14	MF-6	1.19 g/m <sup>2</sup>	137	12.4
I-15	MF-7	1.19 g/m <sup>2</sup>	148	11.5
I-16	MF-8	0.86 g/m <sup>2</sup>	148	4.9
I-17	MF-9	1.20 g/m <sup>2</sup>	143	7.9
I-18	MF-10	1.20 g/m <sup>2</sup>	146	10.5
I-19	MF-11	1.96 g/m <sup>2</sup>	146	7.1

### EXAMPLE 4

10 Photographic coatings were prepared using a very simple hand-coated format comprising a layer as described in Table 1 of Example 1 in which emulsion E-1 was replaced, at the same laydown, by emulsion E-2, a 98% silver bromide, 2% silver iodide, containing tabular emulsion with an equivalent circular diameter of 0.42 microns and a thickness of 0.06 microns. No overcoat layer or 15 hardener was applied to these coatings. The melt formers were incorporated as

solid particle dispersions, similarly prepared to those in earlier examples. The resulting coatings were exposed through a step wedge to a 3.04 log lux light source at 3000K filtered by Daylight 5A, 0.6 Inconel and Wratten 9 filters. The exposure time was 0.1 seconds. After exposure, each coating was thermally processed by contact with a heated platen for 20 seconds. Strips were processed at platen temperatures of 145°C and 150°C in order to check the generality of the effects that were seen. From the density readings at each step, the maximum densities formed were recorded and compared to that formed by MF1 to give a relative measure of melt-former ability. These data are tabulated in Table 7

5 below.

10

TABLE 7

	Dmax	Dmax
	145°C	150°C
MF1	1.24	1.64
MF12	0.50	0.91
MF13	0.29	0.74
MF14 (Comp.)	No image	No image
MF15	1.73	1.80
MF16	1.76	2.23
MF17	1.06	1.75
MF18	No image	0.45
MF19	0.64	1.03

Only MF14 (a comparison) was not effective (inactive) as a melt former. It is thought that the phenol is too sterically hindered to contribute successfully to hydrogen bonding processes necessary for effective melt formation.

15

#### EXAMPLE 5

In a similar experiment to the preceding example, the following maximum density data were obtained.

TABLE 8

	D <sub>max</sub>	D <sub>max</sub>	D <sub>max</sub>
	145°C	150°C	155°C
<b>MF1</b>	0.51	-	1.64
<b>MF20</b>	0.38	1.02	1.78
<b>MF21</b>	No image	No image	Feint Image
<b>MF22</b>	0.19	0.38	1.21

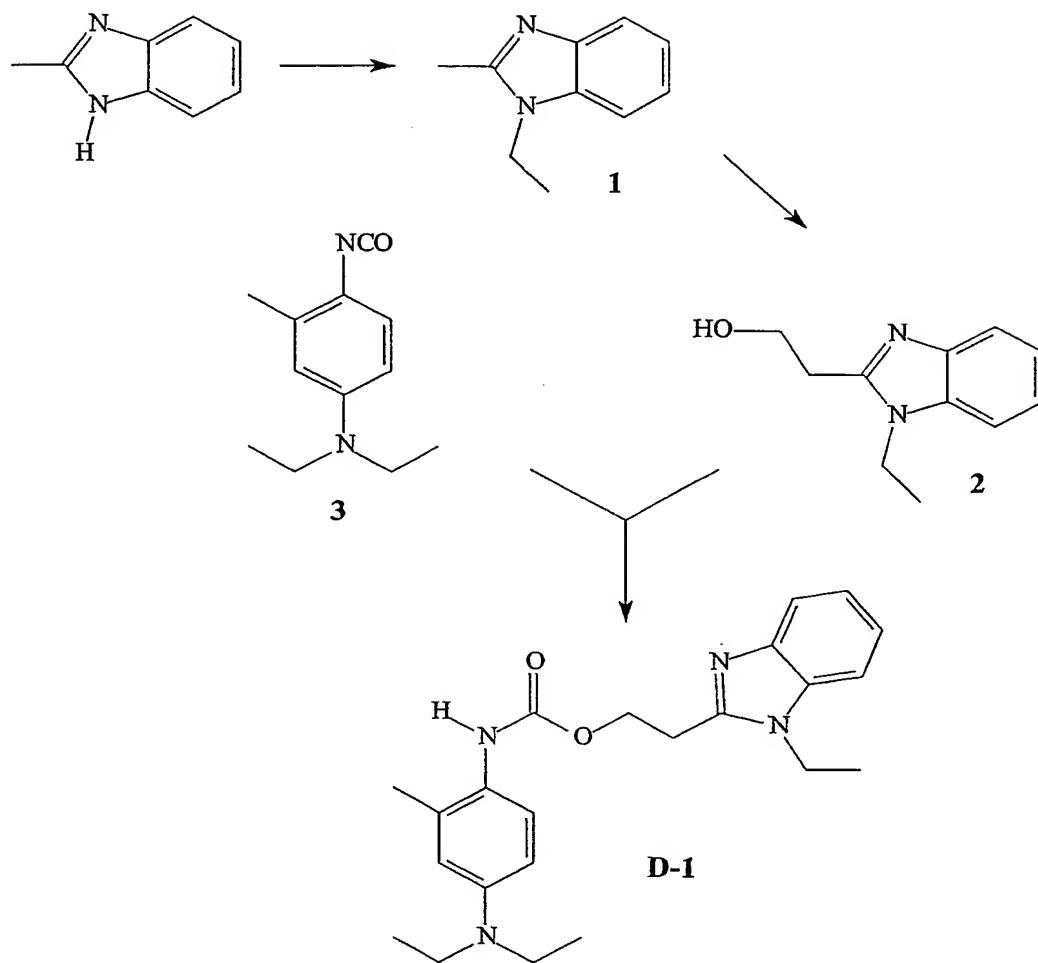
In this experiment, coatings of MF21 showed many large crystals in the coating, which is evidence of recrystallization of the melt former particle 5 dispersion during the coating experiment. The formation of large crystals, because this material was too water soluble, drastically lowered its effectiveness as a melt former. It would be expected to have a high onset temperature because of the low reactivity expected from the large crystals it formed in the coating.

The melt formers, useful in the invention, were either 10 commercially available or simply made in few steps from commercial materials. The following examples describe the synthesis of example blocked compounds useful in the invention.

#### EXAMPLE 6

This Example illustrates the preparation of compound **D-1**, useful 15 in the present invention which is prepared according to the following reaction scheme:

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*Preparation of Intermediate 1:*

To a mixture of KOH (85%) (7.3g, 110 mmol),  $K_2CO_3$  (6.8g, 50 mmol), 2-methylbenzimidazole (Aldrich, 13.2g, 100 mmol) and THF (70 mL) was added at ca. 15 °C diethyl sulfate (11.3 mL, 102 mmol) in 10 mL of THF. After stirring for four hours, 50 mL of ethyl acetate was added, and then the reaction mixture was filtered to remove solid materials. The filtrate was concentrated under reduced pressure to yield 15.5g (97%) of **1** as a yellow oil.

*Preparation of Intermediate 2:*

A pressure bottle was charged with compound **1** (8.0g, 50 mmol), a 38% solution of formaldehyde (12 mL), pyridine (6 mL) and propanol (20 mL) and the reaction mixture was heated at 130 °C for 9 hours. The excess solvent was removed under reduced pressure and the residue recrystallized from ethyl acetate

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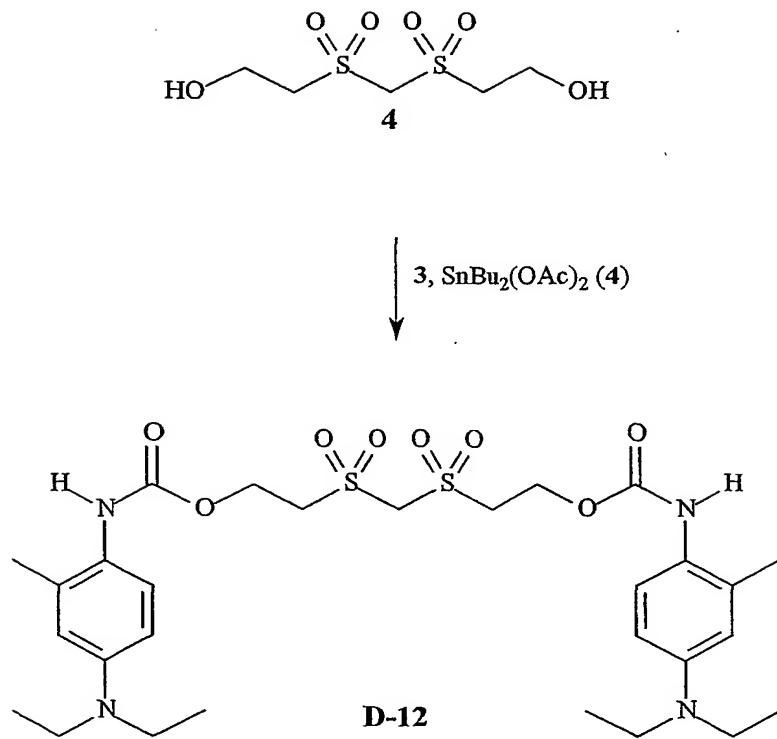
to yield compound **2** (14.5 g, 73%) as a solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.40 (t, 3H, J=7.3 Hz), 3.04 (t, 2H, J=5.3 Hz), 4.10-4.20 (m, 5H), 7.18-7.34 (m, 3H), 7.65-7.72 (m, 1H).

*Preparation of **D-1**:*

5 To a mixture of **2** (5.7g, 30 mmol), dichloromethane (30 mL) and two drops of dibutyltin diacetate was added compound **3**, namely 4-(*N,N*-diethylamino)-2-methylphenyl isocyanate, the latter prepared as described in Brit. Patent 1,152,877, (6.1g, 30 mmol). After being stirred at room temperature for 14 hours the reaction mixture was concentrated under reduced pressure and diluted 10 with ligroin. The precipitated solid material was isolated by filtration to yield **D-1** (9.6g, 81%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.12 (t, 6H, J=7.3 Hz), 1.30-1.46 (m, 3H), 2.18 (s, 3H), 3.20-3.35 (m, 6H), 4.10-4.35 (m, 3H), 4.60-4.68 (m, 3H), 6.18 (bs, 1H), 6.40-6.55 (m, 2H), 7.20-7.44 (m, 4H), 7.69-7.75 (m, 1H).

**EXAMPLE 7**

15 This Example illustrates the preparation of compound **D-12**, or Dev-1, useful in the present invention, which is prepared according to the following reaction scheme:



*Preparation of D-12 (Dev-1):*

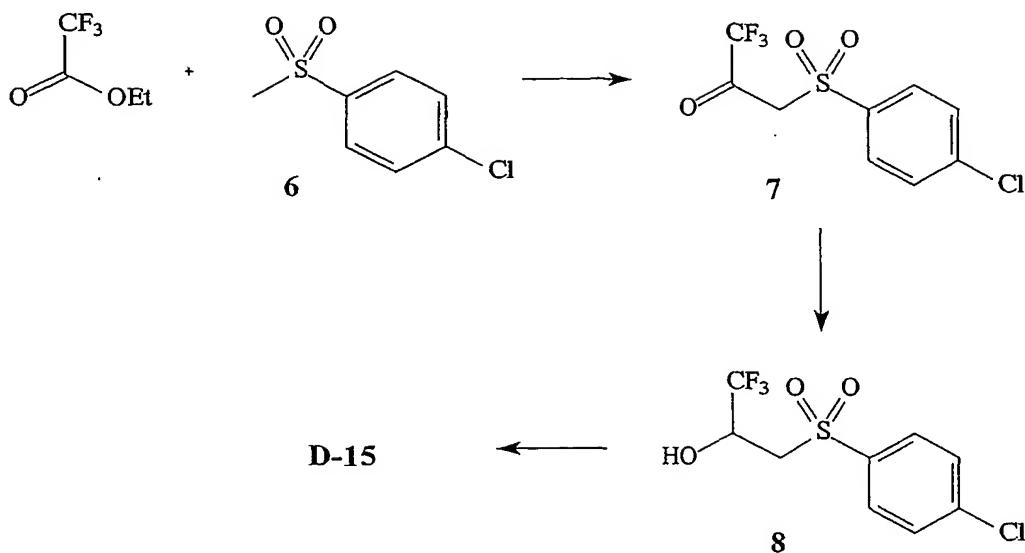
A solution of the diol **4** (15.0 g, 64 mmol), compound **3** (27.0 g, 5 130 mmol) and dibutyltin diacetate (0.05 mL) in 150 mL of tetrahydrofuran was stirred at room temperature for 18 h. The reaction mixture was then filtered through a pad of Celite and the filtrate concentrated *in vacuo*, giving a solid, which was recrystallized from methanol. The yield of **D-12** was 25.0 g (40 mmol, 61%), m.p. 131 °C.

10

**EXAMPLE 8**

This Example illustrates the preparation of compound **D-15**, useful in the present invention, which is prepared according to the following reaction scheme:

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*Preparation of Intermediate 7:*

A solution of sulfone 6 (19.07 g, 100 mmol) in 50 mL of *N,N*-dimethylformamide was added to a suspension of 60% sodium hydride (6.00 g, 150 mmol) in 100 mL of *N,N*-dimethylformamide, the mixture was stirred at 40°C for 90 min and then cooled to 5°C. Neat ethyl trifluoroacetate (36 mL, 300 mmol) was added at 5°C and then the reaction mixture stirred at room temperature for 30 min. The mixture was diluted with 1000 mL of brine and extracted with ether, giving an oil which was purified by column chromatography on silica gel. A solid was obtained which was further purified by crystallization from hexane-isopropyl ether. The yield of 7 was 18.47 g (64 mmol, 64%).

*Preparation of Intermediate 8:*

Solid sodium borohydride (1.89 g, 50 mmol) was added in portions to a solution of 7 (14.33 g, 50 mmol) in 100 mL of methanol and the mixture stirred for 30 min. Water (200 mL) was then added and methanol distilled off. Extraction with ether and removal of the solvent gave 13.75 g (48 mmol, 95%) of 8.

*Preparation of D-15:*

A solution of 7 (13.75 g, 48 mmol, 4-(*N,N*-diethylamino)-2-methylphenyl isocyanate (3,10.21 g, 50 mmol) and dibutyltin diacetate (0.01 mL)

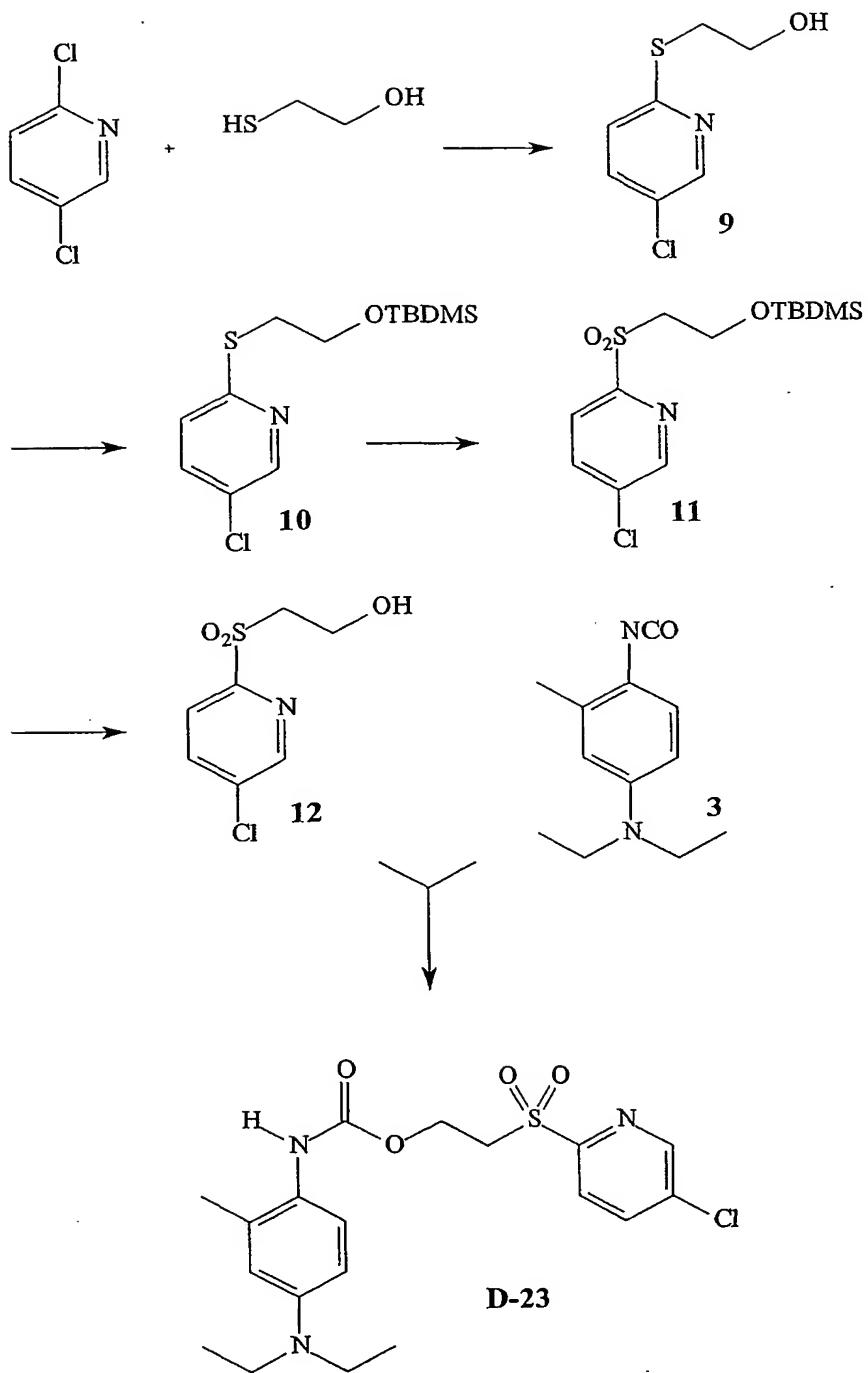
- 103 -

in 50 mL of dichloromethane was stirred at room temperature for 4 days. The solvent was distilled off and the crude product washed with hexane and dried. The yield of **D-15** was 21.00 g (43 mmol, 85%), m.p. 140-143°C.

#### EXAMPLE 9

5 This Example illustrates the preparation of compound **D-23**, useful in the present invention, which is prepared according to the following reaction scheme:

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*Preparation of Intermediate 9:*

A mixture consisting of 2,5-dichloropyridine (Aldrich, 14.80 g, 50 mmol), 2-mercaptopethanol (Fluka, 9.36 g, 120 mmol), potassium carbonate (19.34 g, 140 mmol), and acetone (200 mL) was refluxed for 36 h, cooled to

room temperature and filtered. The filtrate was concentrated in vacuo, dissolved in ether (300 mL) and washed with brine 2 x 100 mL). The organic solution was concentrated and the crude product purified by column chromatography on silica gel with heptane / ethyl acetate. The yield of **9** was 12.05 g (64 mmol, 64%).

5 *Preparation of Intermediate 10:*

Solid *tert*-butyldimethylsilyl chloride (Aldrich, TBDMSCl, 11.34 g, 75 mmol) was added in one portion to a solution of **9** (11.86 g, 62.5 mmol) and imidazole (5.97 g, 87.5 mmol) in tetrahydrofuran (160 mL), stirred at 5°C. Following the addition, the mixture was stirred at room temperature for 20 h and 10 then worked up with saturated aqueous sodium bicarbonate and ether. The product was purified by column chromatography on silica gel with heptane / ethyl acetate. The yield of **10** was 17.69 g (58 mmol, 93%).

*Preparation of Intermediate 11:*

A solution of *meta*-chloroperbenzoic acid (mCPBA, 77%, 27.01 g, 15 120 mmol) in dichloromethane (150 mL) was added in drops over a period of 30 min to a solution of **10** in dichloromethane (200 mL), stirred at 5°C. Following the addition the mixture was stirred at room temperature for 22 h and quenched with saturated aqueous sodium bicarbonate, followed by extraction with dichloromethane and column chromatography (silica, heptane / dichloromethane) 20 which gave 11.67 g (35 mmol, 87%) of **11**.

*Preparation of Intermediate 12:*

A solution of **11** (10.08 g, 30 mmol) in tetrahydrofuran (90 mL) / water (90 mL) / acetic acid (270 mL) was kept at room temperature for 4 days. The solvents were distilled off and the residue crystallized from heptane / 25 isopropyl ether. The yield of **12** was 6.41 g (29 mmol, 96%).

*Preparation of D-23:*

A solution of **12** (4.43 g, 20 mmol) and compound **3**, namely 4-(*N,N*-diethylamino)-2-methylphenyl isocyanate, the latter prepared as described in Brit. Patent 1,152,877 (4.08 g, 20 mmol), and dibutyltin diacetate (0.01 mL) was 30 stirred in 35 mL of tetrahydrofuran at room temperature for 24 hours. The

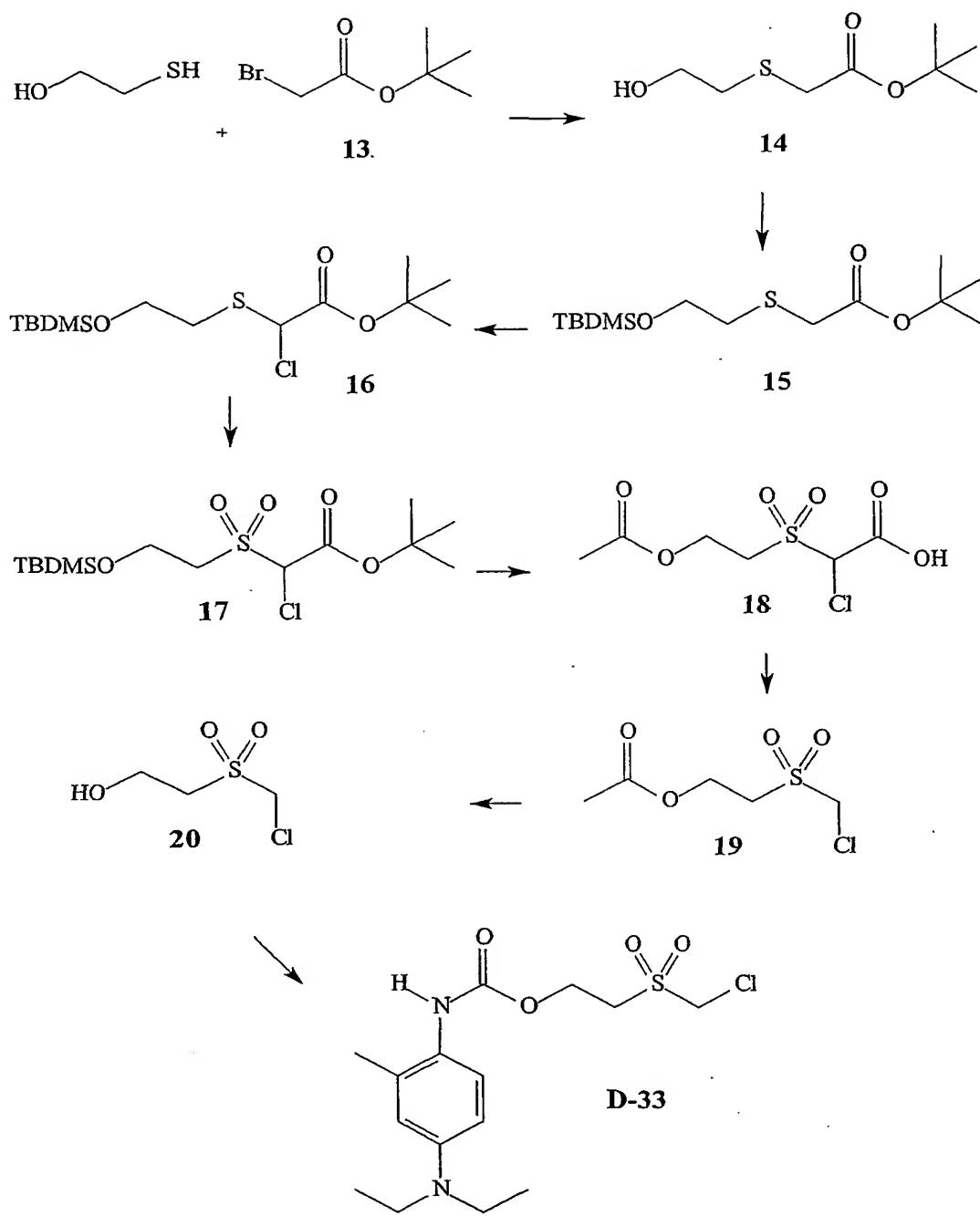
- 106 -

solvent was distilled off and the crude oily product stirred with 50 mL of isopropyl ether, giving colorless crystals of **D-23** (8.18 g, 19.2 mmol, 96%), m.p. 84-85°C.

#### EXAMPLE 10

5 This Example illustrates the preparation of compound **D-33**, useful in the present invention, which is prepared according to the following reaction scheme:

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*Preparation of Intermediate 14:*

A solution of t-butyl bromoacetate **13** (Aldrich, 19.51 g, 100 mmol) in 100 mL of acetonitrile was added in drops over a period of 30 min to a cooled (5°C) solution of 2-mercaptopropanoic acid (8.19 g, 105 mmol) in 100 mL of acetonitrile, containing potassium carbonate (15.20 g, 110 mmol). Following the

addition the mixture was stirred at room temperature for 3 h and filtered. The filtrate was diluted with 200 mL of ether and washed with brine (50 mL). The ethereal solution was dried over sodium sulfate and concentrated in vacuo to give 19.24 g of **14** (100 mmol, 100%).

5 *Preparation of Intermediate 15:*

Solid *tert*-butyldimethylsilyl chloride (TBDMSCl, 18.09 g, 120 mmol) was added in one portion to a solution of **14** (19.24 g, 100 mmol) and imidazole (9.55 g, 140 mmol) in 250 mL of tetrahydrofuran, stirred under nitrogen. After 2 h at room temperature the mixture was quenched with 200 mL 10 of saturated aqueous sodium bicarbonate and extracted with ether. The crude product was filtered through silica gel (ether/heptane) giving 29.21 g (95 mmol, 95%) of **15**.

*Preparation of Intermediate 16:*

Solid N-chlorosuccinimide (6.68 g, 50 mmol) was added in 15 portions over a period of 30 min to a solution of **15** (15.33 g, 50 mmol) in 100 mL of carbon tetrachloride that was stirred at 5°C. The reaction was run for 2 h and filtered. Removal of the solvent left 17.44 g of **16** as an oil (50 mmol, 100%).

*Preparation of Intermediate 17:*

20 A solution of m-chloroperbenzoic acid (mCPBA, 77%, 24.75 g, 110 mmol) in 200 mL of dichloromethane was added in drops over a period of 30 min to a solution of **16** (17.44 g, 50 mmol) in 100 mL of dichloromethane, stirred at 5°C. Following the addition, the mixture was stirred at 5°C for 2 h and then at room temperature for 1 h. The reaction was quenched with saturated aqueous 25 sodium bicarbonate (250 mL) and the organic layer was dried and concentrated giving 18.66 g of **17** as an oil (50 mmol, 100%).

*Preparation of Intermediate 18:*

A solution of **17** (11.26 g, 30.2 mmol), acetic anhydride (5 mL) and p-toluenesulfonic acid monohydrate (100 mg) in acetic acid (150 mL) was 30 refluxed for 1 h. The solution was cooled to room temperature, diluted with 100

mL of water and stirred for 2 h. A solid was filtered off and the filtrate was concentrated in vacuo to produce **18** as a colorless oil.

*Preparation of Intermediate 19:*

5 A solution of crude **18** and sodium acetate (2.46 g, 30 mmol) in acetic acid (30 mL) was refluxed for 15 min, cooled to room temperature and the solvent was distilled off. The residue was worked up with water and ethyl acetate, giving 5.66 g of **19** as an oil.

*Preparation of Intermediate 20:*

10 A solution of crude **19** and concentrated hydrochloric acid (0.5 mL) in 75 mL of methanol was stirred at room temperature for 3 days. The solvent was distilled off leaving 4.61 g of **20** (29 mmol, 96% based on **17**).

*Preparation of D-33:*

15 A solution of **20** (1.59 g, 10 mmol), **3** (2.25 g, 11 mmol) and dibutyltin diacetate (0.02 mL) in acetonitrile (10 mL) was kept at room temperature in a stoppered flask for 24 h. The solvent was removed giving an oil which crystallized when stirred with isopropyl ether. The solid was collected, washed with isopropyl ether and dried. The yield of **D-33** was 3.03 g (8.3 mmol, 83%), m.p. 96-98°C, ESMS: ES<sup>+</sup>, m/z 363 (M+1, 95%).

### EXAMPLE 11

20 This Example illustrates a multilayer photographic element containing a phenolic melt former, in this case salicylanilide.

*Silver Halide Emulsions:*

25 The emulsions employed in these examples are all silver iodobromide tabular grains precipitated by conventional means as known in the art. Table 9 below lists various emulsions prepared, along with their iodide content (the remainder assumed to be bromide), their dimensions, and the sensitizing dyes used to impart spectral sensitivity. All of these emulsions have been given chemical sensitizations as known in the art to produce optimum sensitivity.

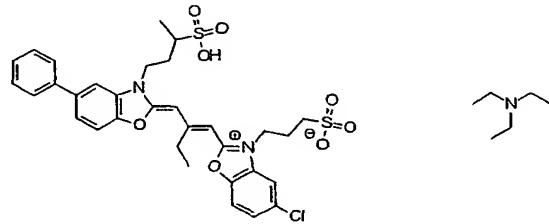
TABLE 9

Emulsion	Spectral sensitivity	Iodide content (%)	Diameter (μm)	Thickness (μm)	Dyes
EY-3	Yellow	2	1.23	0.125	SY-1
EY-4	yellow	2	0.45	0.061	SY-1
EY-5	yellow	2	0.653	0.093	SY-1
EM-3	magenta	2	1.23	0.125	SM-1 + SM-3
EM-4	magenta	2	0.45	0.061	SM-1 + SM-3
EM-5	magenta	2	0.653	0.093	SM-1 + SM-3
EC-3	cyan	2	1.23	0.125	SC-1 + SC-2
EC-4	cyan	2	0.45	0.061	SC-1 + SC-2
EC-5	cyan	2	0.653	0.093	SC-1 + SC-2

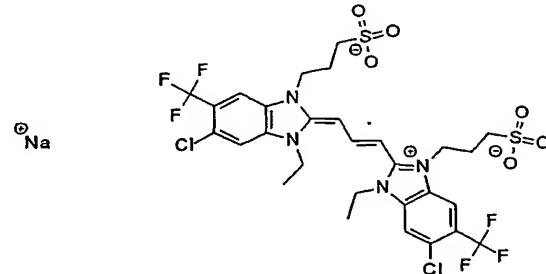
In addition to the components described in the previous examples, the following components were used, including a list of the chemical structures.

5

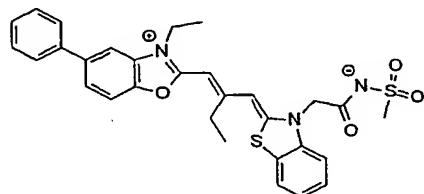
SM-1

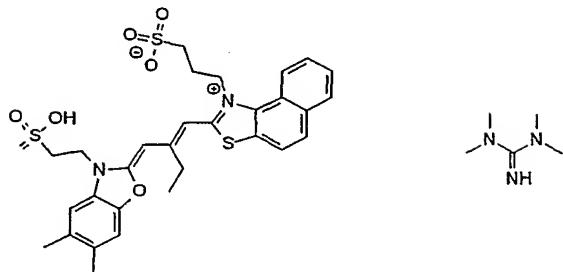
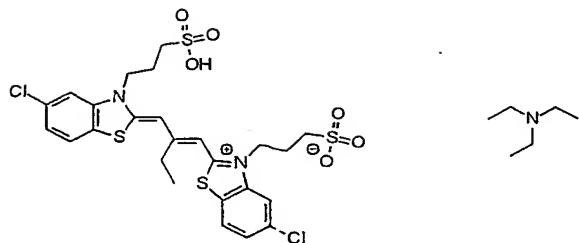


SM-2



SM-3





Coupler Dispersion CDM-2:

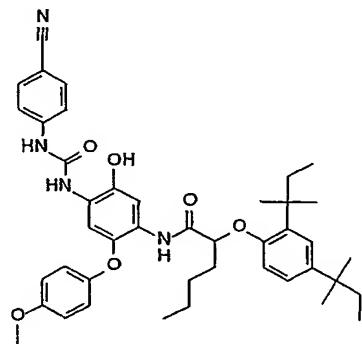
A coupler dispersion was prepared by conventional means containing coupler M-1 without any additional permanent solvents.

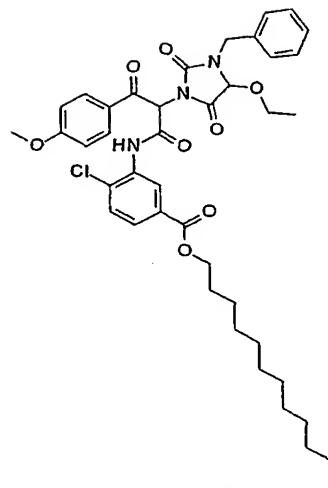
## 5 *Coupler Dispersion CDC-1:*

An oil based coupler dispersion was prepared by conventional means containing coupler C-1 and dibutyl phthalate at a weight ratio of 1:2.

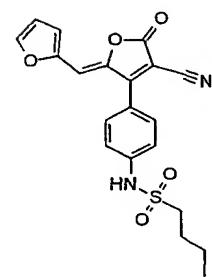
### *Coupler Dispersion CDY-1:*

An oil based coupler dispersion was prepared by conventional means containing coupler Y-1 and dibutyl phthalate at a weight ratio of 1:0.5.

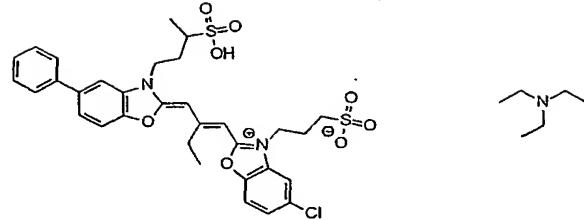




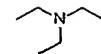
Y-1



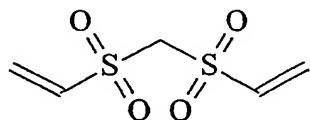
SY-1



SM-1



Hardener-1



A multilayer imaging element as described in Table 10 below was created to show sufficient image formation capability to allow for use in full color photothermographic elements intended for capturing live scenes. The multilayer element of this example produced an image prior to any wet processing steps.

5

TABLE 10

Overcoat	1.1 g/m <sup>2</sup> Gelatin 0.32 g/m <sup>2</sup> Hardener-1
Fast Yellow	0.54 g/m <sup>2</sup> AgBrI from emulsion EY-3 0.17 g/m <sup>2</sup> silver benzotriazole from SS-1 0.17 g/m <sup>2</sup> silver-1-phenyl-5-mercaptotetrazole from SS-2 0.29 g/m <sup>2</sup> coupler Y-1 from dispersion CDY-1 0.46 g/m <sup>2</sup> Developer Dev-1 0.46 g/m <sup>2</sup> Salicylanilide 2.3 g/m <sup>2</sup> Gelatin
Slow Yellow	0.27 g/m <sup>2</sup> AgBrI from emulsion EY-4 0.16 g/m <sup>2</sup> AgBrI from emulsion EY-5 0.15 g/m <sup>2</sup> silver benzotriazole from SS-1 0.15 g/m <sup>2</sup> silver-1-phenyl-5-mercaptotetrazole from SS-2 0.25 g/m <sup>2</sup> coupler Y-1 from dispersion CDY-1 0.40 g/m <sup>2</sup> Developer Dev-1 0.40 g/m <sup>2</sup> Salicylanilide 2.0 g/m <sup>2</sup> Gelatin
Yellow Filter	0.08 g/m <sup>2</sup> SY-1 1.07 g/m <sup>2</sup> Gelatin
Fast Magenta	0.54 g/m <sup>2</sup> AgBrI from emulsion EM-3 0.17 g/m <sup>2</sup> silver benzotriazole from SS-1 0.17 g/m <sup>2</sup> silver-1-phenyl-5-mercaptotetrazole from SS-2 0.29 g/m <sup>2</sup> coupler M-1 from dispersion CDM-2 0.46 g/m <sup>2</sup> Developer Dev-1 0.46 g/m <sup>2</sup> Salicylanilide 2.3 g/m <sup>2</sup> Gelatin
Slow Magenta	0.27 g/m <sup>2</sup> AgBrI from emulsion EM-4 0.16 g/m <sup>2</sup> AgBrI from emulsion EM-5 0.15 g/m <sup>2</sup> silver benzotriazole from SS-1 0.15 g/m <sup>2</sup> silver-1-phenyl-5-mercaptotetrazole from SS-2 0.25 g/m <sup>2</sup> coupler M-1 from dispersion CDM-2 0.40 g/m <sup>2</sup> Developer Dev-1 0.40 g/m <sup>2</sup> Salicylanilide 2.0 g/m <sup>2</sup> Gelatin
Interlayer	1.07 g/m <sup>2</sup> Gelatin
Fast Cyan	0.54 g/m <sup>2</sup> AgBrI from emulsion EC-3 0.17 g/m <sup>2</sup> silver benzotriazole from SS-1 0.17 g/m <sup>2</sup> silver-1-phenyl-5-mercaptotetrazole from SS-2 0.29 g/m <sup>2</sup> coupler C-1 from dispersion CDC-1 0.46 g/m <sup>2</sup> Developer Dev-1 0.46 g/m <sup>2</sup> Salicylanilide 2.3 g/m <sup>2</sup> Gelatin

Slow Cyan	0.27 g/m <sup>2</sup> AgBrI from emulsion EC-4 0.16 g/m <sup>2</sup> AgBrI from emulsion EC-5 0.15 g/m <sup>2</sup> silver benzotriazole from SS-1 0.15 g/m <sup>2</sup> silver-1-phenyl-5-mercaptotetrazole from SS-2 0.25 g/m <sup>2</sup> coupler C-1 from dispersion CDC-1 0.40 g/m <sup>2</sup> Developer Dev-1 0.40 g/m <sup>2</sup> Salicylanilide 2.0 g/m <sup>2</sup> Gelatin
Antihalation Layer	0.05 g/m <sup>2</sup> Carbon 1.6 g/m <sup>2</sup> Gelatin
Support	Polyethylene terephthalate support (7 mil thickness)

The resulting coating was exposed through a step wedge to a 1.8 log lux light source at 5500K and Wratten 2B filter. The exposure time was 0.1 seconds. After exposure, the coating was thermally processed by contact with a 5 heated platen for 20 seconds at 145°C. Cyan, magenta, and yellow densities were read using status M color profiles, to yield the densities listed in Table 11 below. It is clear from these densities that to coating serves as a useful photographic element capturing multicolor information.

TABLE 11

Record	Dmin	Dmax
Cyan	0.38	1.47
Magenta	0.72	2.65
Yellow	0.68	1.80

10 The film element was further loaded into a single lens reflex camera equipped with a 50 mm / f 1.7 lens. The exposure control of the camera was set to ASA 100 and a live scene indoors without the use of a flash was captured on the above element. The element was developed by heating for 20 seconds at 145°C and no subsequent processing was done to the element.

15 The resulting image was scanned with a Nikon® LS2000 film scanner. The digital image file thus obtained was loaded into Adobe Photoshop® (version 5.0.2) where corrections were made digitally to modify tone scale and color saturation, thus rendering an acceptable image. The image was viewed as 20 softcopy by means of a computer monitor. The image file was then sent to a

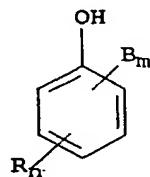
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Kodak 8650 dye sublimation printer to render a hardcopy output of acceptable quality.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

**WHAT IS CLAIMED IS:**

1. A color photothermographic element comprising at least three light-sensitive units which have their individual sensitivities in different wavelength regions, each of the units comprising at least one light-sensitive silver-halide emulsion, binder, and dye-providing coupler, and a blocked developer in the presence of an effective amount of a thermal solvent represented by the following structure



wherein the substituent B is independently selected from a substituent where an oxygen, carbon, nitrogen phosphorus or sulfur atom is linked to the ring as part of an ester, amido, ether, aminosulfonyl, sulfamoyl, carbonyl, (acyl) or sulfonyl group;

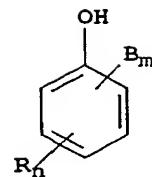
m is 0 to 4; and

wherein the substituent R is independently selected from a substituted or unsubstituted alkyl, cycloalkyl, aryl, alkylaryl, or forms a ring with another substituent on the ring;

n is 0 to 4; and

wherein m+n is 1 to 5.

2. A color photothermographic element comprising at least three light-sensitive units which have their individual sensitivities in different wavelength regions, each of the units comprising at least one light-sensitive silver-halide emulsion, binder, and dye-providing coupler, and a blocked developer in the presence of a thermal solvent having a melting point of at least 80°C, represented by the following structure



wherein the substituent B is independently selected from a substituent where an oxygen, carbon, nitrogen, phosphorus or sulfur atom is linked to the ring as part of a ketone, aldehyde, ester, amido, carbamate, ether, aminosulfonyl, sulfamoyl, sulfonyl, amine, phosphine, or aromatic heterocyclic group;

m is 0 to 4; and

wherein the substituent R is independently selected from a substituted or unsubstituted alkyl, cycloalkyl, aryl, alkylaryl, or forms a ring with another substituent on the ring;

n is 0 to 4; and

wherein m+n is 1 to 5.

3. The color photothermographic element of claim 1 wherein B is selected from the group consisting of  $-C(=O)NHR^2$ ,  $-NHC(=O)R^2$ ,  $-NHSO_2R^2$ ,  $-COR^2$ ,  $-SO_2NHR^2$ , and  $-SO_2R^2$  wherein  $R^2$  is substituted or unsubstituted alkyl, cycloalkyl, aryl, alkylaryl, heterocyclic group and can optionally comprise a phenolic hydroxyl group.

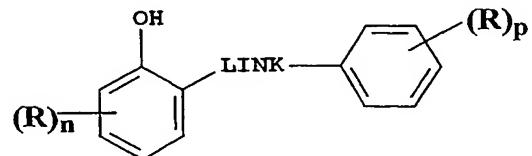
4. The color photothermographic element of claim 2 wherein B is selected from the group consisting of  $-C(=O)NHR^2$ ,  $-NHC(=O)R^2$ ,  $-NHSO_2R^2$ ,  $-SO_2NHR^2$ ,  $-SO_2R^2$ ,  $-C(=O)R^2$ ,  $-C(=O)OR^2$ , and  $-OR^2$ , wherein  $R^2$  is substituted or unsubstituted alkyl, cycloalkyl, aryl, alkylaryl, heterocyclic group and can optionally comprise a phenolic hydroxyl group.

5. The color photothermographic element of claim 2 wherein the melting point is between 100 and 250°C.

6. The color photothermographic element of claim 2 wherein when m is 0, n is at least 1 and there is a second phenolic group on an R substituent.

7. The color photothermographic element of claim 3 wherein n is 1 and R<sup>2</sup> is a substituted or unsubstituted phenyl substituent.

8. The color photothermographic element of claim 2 wherein the melt former has the following structure:



wherein LINK is selected from the group consisting of -C(=O)NH-, -NHC(=O)-, -NHSO<sub>2</sub>-, -C(=O)-, -C(=O)O-, -O(R<sup>3</sup>)-, -SO<sub>2</sub>NH-, and -SO<sub>2</sub>-, where R<sup>3</sup> is an alkyl group and R and n is as defined above; and p is 0 to 4.

9. The color photothermographic element of claim 8 wherein R is independently selected from substituted or unsubstituted C1 to C10 alkyl group.

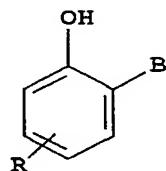
10. The color photothermographic element of claim 2 wherein n+p is 1 and R is a C1 to C6 alkyl group.

11. The color photothermographic element of claim 1 wherein the thermal solvent is 2-hydroxybenzamide or a derivative thereof.

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12. The color photothermographic element of claim 1 in which the thermal solvent is present in the amount of 0.01times to 0.5 times the amount by weight of coated gelatin per square meter.

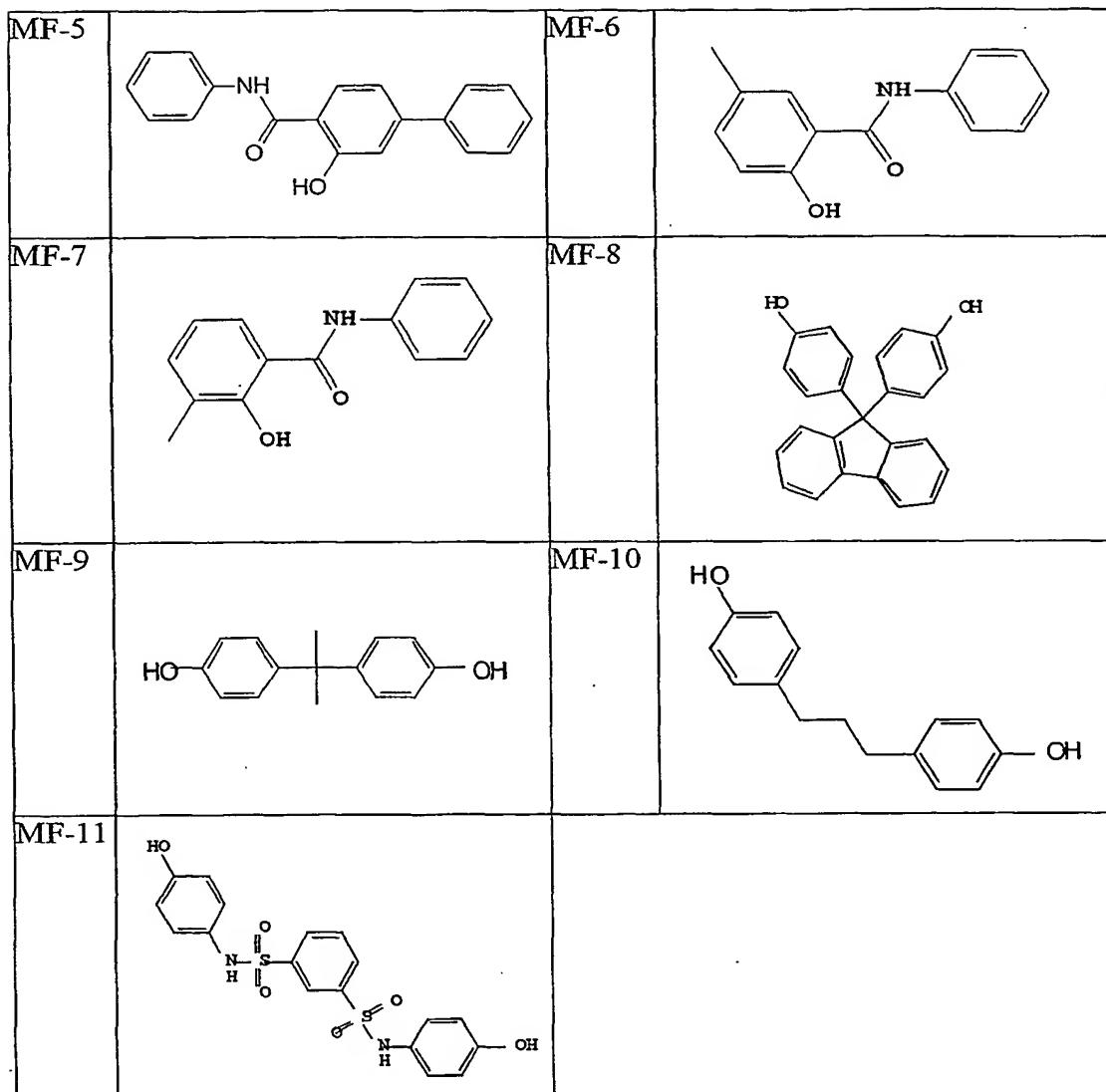
13. The color photothermographic element of claim 1, comprising a radiation sensitive silver halide, and a thermal solvent represented by the following structure



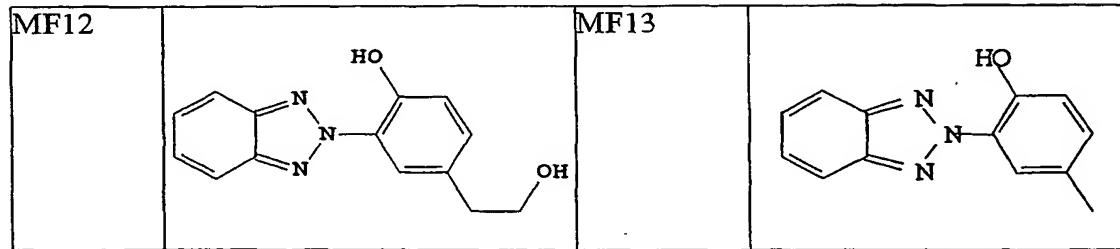
wherein B and R are as described in claim 1.

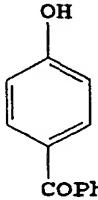
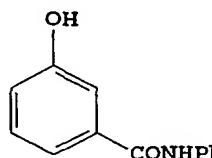
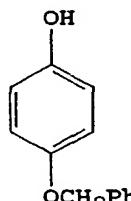
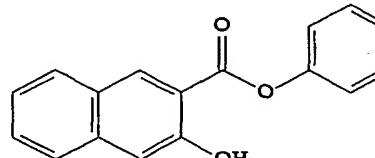
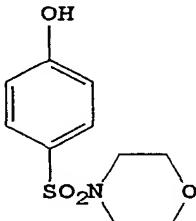
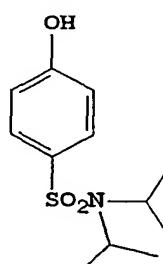
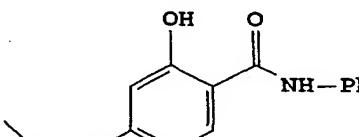
14. The photothermographic element of claim 3 wherein the thermal solvent is selected from the group consisting of:

MF-1		MF-2	
MF-3		MF-4	

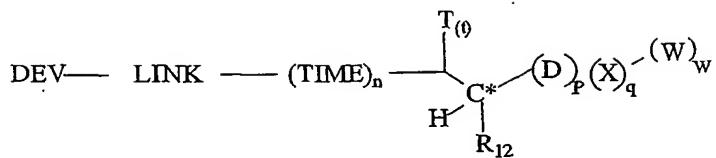


15. The photothermographic element of claim 2 wherein the thermal solvent is selected from the group consisting of:



MF15		MF17	
MF16			
MF18		MF19	
MF20			
MF22			

16. A color photothermographic element according to claim 1, wherein the blocked developer is a compound represented by the following structure:



wherein:

DEV is a developing agent;

LINK is a linking group;

TIME is a timing group;

n is 0, 1, or 2;

t is 0, 1, or 2, and when t is not 2, the necessary number of hydrogens ( $2-t$ ) are present in the structure;

$C^*$  is tetrahedral ( $sp^3$  hybridized) carbon;

p is 0 or 1;

q is 0 or 1;

w is 0 or 1;

$p + q = 1$  and when p is 1, q and w are both 0; when q is 1, then w is 1;

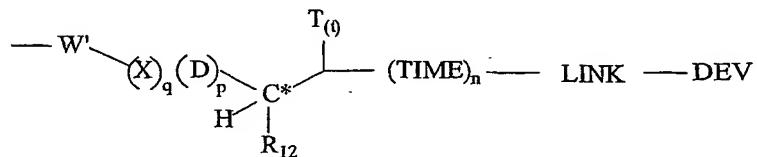
$R_{12}$  is hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, aryl or heterocyclic group or  $R_{12}$  can combine with W to form a ring;

T is independently selected from a substituted or unsubstituted (referring to the following T groups) alkyl group, cycloalkyl group, aryl, or heterocyclic group, an inorganic monovalent electron withdrawing group, or an inorganic divalent electron withdrawing group capped with at least one C1 to C10 organic group (either an  $R_{13}$  or an  $R_{13}$  and  $R_{14}$  group), preferably capped with a substituted or unsubstituted alkyl or aryl group; or T is joined with W or  $R_{12}$  to form a ring; or two T groups can combine to form a ring;

D is a first activating group selected from substituted or unsubstituted (referring to the following D groups) heteroaromatic group or aryl group or monovalent electron withdrawing group, wherein the heteroaromatic can optionally form a ring with T or  $R_{12}$ ;

X is a second activating group and is a divalent electron withdrawing group;

W is W' or a group represented by the following structure:



W' is independently selected from a substituted or unsubstituted (referring to the following W' groups) alkyl (preferably containing 1 to 6 carbon atoms), cycloalkyl (including bicycloalkyls, but preferably containing 4 to 6 carbon atoms), aryl (such as phenyl or naphthyl) or heterocyclic group; and wherein W' in combination with T or R<sub>12</sub> can form a ring;

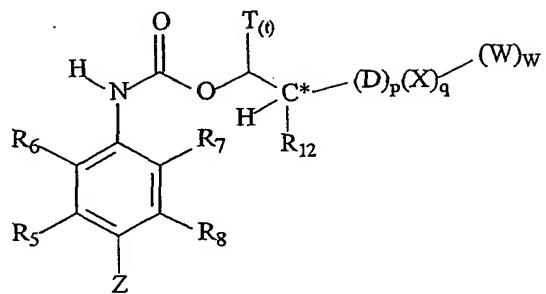
R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, and R<sub>16</sub> can independently be selected from substituted or unsubstituted alkyl, aryl, or heterocyclic group;

any two members of the following set: R<sub>12</sub>, T, and either D or W, that are not directly linked may be joined to form a ring, provided that creation of the ring will not interfere with the functioning of the blocking group;

wherein the T, R<sub>12</sub>, D, X and W groups are selected such that the blocked developer has a half-life (t<sub>1/2</sub>) ≤ 20 min, and a peak discrimination, at a temperature of at least 60°C, of at least 2.0.

17. The photothermographic element of claim 1 wherein D<sub>p</sub> is 3 to 10 and D<sub>p</sub> is at a temperature of 100 to 160°C.

18. A color photothermographic element according to claim 16, wherein the blocked developer is a compound represented by the following structure:

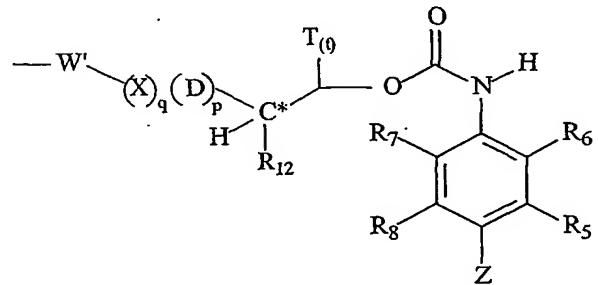


wherein:

Z is OH or NR<sub>2</sub>R<sub>3</sub>, where R<sub>2</sub> and R<sub>3</sub> are independently hydrogen or a substituted or unsubstituted alkyl group or R<sub>2</sub> and R<sub>3</sub> are connected to form a ring;

R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, and R<sub>8</sub> are independently hydrogen, halogen, hydroxy, amino, alkoxy, carbonamido, sulfonamido, alkylsulfonamido or alkyl, or R<sub>5</sub> can connect with R<sub>3</sub> or R<sub>6</sub> and/or R<sub>8</sub> can connect to R<sub>2</sub> or R<sub>7</sub> to form a ring;

W is either W' or a group represented by the following structure:



wherein T, t, C\*, R<sub>12</sub>, D, p, X, q, W' and w are as defined above.

19. A photothermographic element according to claim 18, wherein X is a sulfonyl or a cyano group and Z is NR<sub>2</sub>R<sub>3</sub>.

20. A photothermographic element according to claim 18, wherein when T is an electron withdrawing group or a heteroaromatic group, or an aryl substituted with one or more electron withdrawing groups.

21. A photothermographic element according to claim 18, wherein when T is  $-\text{SO}_2-$ ,  $-\text{OSO}_2-$ ,  $-\text{NR}_{14}(\text{SO}_2)-$ ,  $-\text{CO}_2-$ ,  $-\text{CCl}_2-$ , or  $-\text{NR}_{14}(\text{C=O})-$  group capped with a substituted or unsubstituted alkyl, aryl, or heteroaromatic group.

22. A photothermographic element according to claim 18, wherein T is a trifluoromethyl group, 2-nitrophenyl group, a thiienyl group or a furyl group.

23. A photothermographic element according to claim 1 wherein the photothermographic element contains an imaging layer comprising, in addition to the blocked developer, a light sensitive silver halide emulsion, and a non-light sensitive silver salt oxidizing agent.

24. A photothermographic element according to claim 1 that is capable of dry development without the application of aqueous solutions.

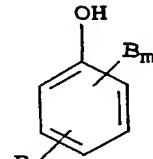
25. A photothermographic element according to claim 1 comprising a melt former for the blocked developer.

26. A photothermographic element according to claim 1 comprising a mixture of at least two organic silver salts, at least one of which is a non-light sensitive silver salt oxidizing agent.

27. A photothermographic element according to claim 1 that does not comprise an effective amount of a basic metal compound slightly soluble in water for unblocking the blocked developer.

28. A photothermographic element according to claim 1 wherein the imaging layer does not have a pH of more than 7, even in the presence of water.

29. A method of image formation comprising the step of developing an imagewise exposed photothermographic element comprising at least three light-sensitive units which have their individual sensitivities in different wavelength regions, each of the units comprising at least one light-sensitive silver-halide emulsion, binder, and dye-providing coupler, and a blocked developer having a half-life ( $t_{1/2}$ )  $\leq 20$  min, and a peak discrimination, at a temperature of at least 60°C, of at least 2.0, which blocked developer and coupler is developed in the presence of a thermal solvent having the following formula:



I

wherein the substituent B is independently selected from a substituent where an oxygen, carbon, nitrogen phosphorus or sulfur atom is linked to the ring as part of a ketone, aldehyde, ester, amido, carbamate, ether, aminosulfonyl, sulfamoyl, sulfonyl, amine, phosphine, or aromatic heterocyclic group;

m is 0 to 4; and

wherein the substituent R is independently selected from a substituted or unsubstituted alkyl, cycloalkyl, aryl, alkylaryl, or forms a ring with another substituent on the ring;

n is 0 to 4; and

wherein m+n is 1 to 5.

30. The method of claim 29 wherein the substituent B is linked to the ring as part of an ester, amido, ether, aminosulfonyl, sulfamoyl, sulfonyl or sulfone group;

31. The method of claim 29 wherein D<sub>p</sub> is 3 or greater and D<sub>p</sub> is at a temperature of 100 to 160°C.

32. A method according to claim 29, wherein said developing comprises treating said imagewise exposed element at a temperature between about 80°C and about 180°C for a time ranging from about 0.5 to about 60 seconds.

33. A method according to claim 29, wherein said developing comprises treating said imagewise exposed element to a volume of processing solution is between about 0.1 and about 10 times the volume of solution required to fully swell the photographic element.

34. A method according to claim 29, wherein the developing is accompanied by the application of a laminate sheet containing additional processing chemicals.

35. A method according to claim 29, wherein the applied processing solution is a base, acid, or pure water.

36. A method according to claim 29 wherein image formation comprises the step of scanning an imagewise exposed and developed imaging element to form a first electronic image representation of said imagewise exposure.

37. A method according to claim 29 wherein the image formation comprises the step of digitizing a first electronic image representation formed from an imagewise exposed, developed, and scanned imaging element to form a digital image.

38. A method according to claim 29 wherein image formation comprising the step of modifying a first electronic image representation formed from and imagewise exposed, developed, and scanned imaging element formulated to form a second electronic image representation.

39. A method according to claim 29 comprising storing, transmitting, printing, or displaying an electronic image representation of an image derived from an imagewise exposed, developed, scanned imaging element.

40. A method according to claim 39, wherein printing the image is accomplished with any of the following printing technologies: electrophotography; inkjet; thermal dye sublimation; or CRT or LED printing to sensitized photographic paper.

41. A method according to claim 39 wherein the photothermographic element contains an imaging layer comprising, in addition to the blocked developer, a light sensitive silver halide emulsion, and a non-light sensitive silver salt oxidizing agent.

42. A method according to claim 29 wherein the developing is accomplished in a dry state without the application of aqueous solutions.

43. A method according to claim 29 wherein the melt former has a melting point of at least 100°C.

44. A method according to claim 29 wherein the melt former has a melting point of at least 100°C but melts at the temperature of development to obtain image formation.

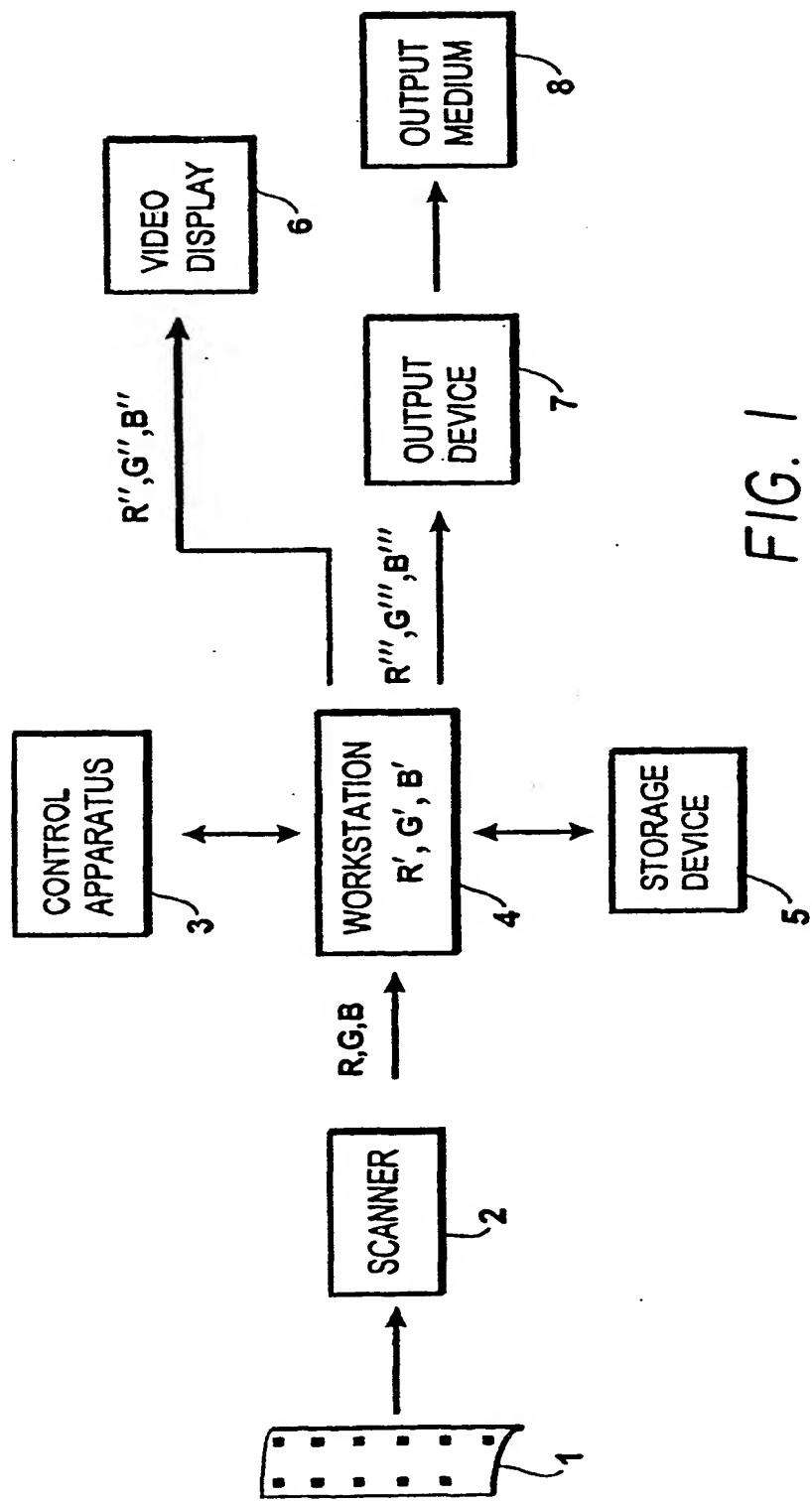


FIG. 1

